ORGANOMETALLICS

Early-transition-metal ketenimine complexes. Synthesis, reactivity and structural characterization of complexes with .eta.2(C,N)-ketenimine groups bound to the halobis[(trimethylsilyl)cyclopentadienyl]niobium unit. X-ray structure of Nb(.eta.5-C5H4SiMe3)2Cl(.eta.2(C,N)-PhN:C:CPh2)

Antonio Antinolo, Mariano Fajardo, Carmen Lopez Mardomingo, Antonio Otero, Youssef Mourad, Yves Mugnier, Julia Sanz-Aparicio, Isabel Fonseca, and Feliciana Florencio

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Table XI. Selected Bond Lengths (Å) and Angles (deg) for 8

Distances			
Ru(1)-Ru(2)	2.879 (2)	Ru(1)-Ru(3)	2.841 (4)
Ru(2)-Ru(4)	2.993 (4)	Ru(3)-Ru(4)	2.897 (3)
Ru(1)-P(1)	2.495 (7)	Ru(2)-P(1)	2.351 (7)
Ru(3)-P(1)	2.478 (7)	Ru(4)-P(1)	2.348 (7)
Ru(1)-C(1)	2.30 (3)	Ru(2)-C(1)	2.10 (3)
Ru(3)-C(2)	2.32 (3)	Ru(4)-C(2)	2.10 (2)
Ru(1)-C(9)	2.01 (3)	Ru(3)-C(9)	1.99 (3)

Angles			
Ru(1)-C(1)-Ru(2)	81.4 (9)	Ru(1)-C(1)-C(2)	108 (2)
Ru(2)-C(1)-C(2)	110 (2)	Ru(3)-C(2)-Ru(4)	81.8 (8)
Ru(3)-C(2)-C(1)	107 (2)	Ru(4)-C(2)-C(1)	113 (2)
Ru(1)-C(9)-Ru(3)	90 (1)		

those incorporated in SHELX.[34] Data solution and refinement were performed with the SHELX program system on the University of Adelaide's VAX11/780 computer system.

Atomic positions for the complexes 4-8 are given in Tables II-VI and selected bond distances and angles in Tables VII-XI.

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Supplementary Material Available: Tables of bond lengths and angles and thermal parameters for complexes 4-8, together with tables of H atom positions and thermal parameters for compounds 5-7 (27 pages); listings of observed and calculated structure factors for complexes 4-8 (94 pages). Ordering information is given on any current masthead page.

Early-Transition-Metal Ketenimine Complexes. Synthesis, Reactivity, and Structural Characterization of Complexes with $\eta^2(C,N)$-Ketenimine Groups Bound to the Halogenobis((trimethylsilyl)cyclopentadienyl)niobium Unit. X-ray Structure of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,N)\text{-}PhN{=}C{=}CPh_2)$

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Received January 5, 1990

The reaction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X$ (X = Cl, Br) with 1 equiv of various ketenimines, $R^1N{=}C{=}CR^2R^3$, leads to the niobium derivatives $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}R^1N{=}C{=}CR^2R^3)$ (**1**, X = Cl, $R^1 = R^2 = R^3 = C_6H_5$; **2**, X = Cl, R^1 = p-CH_3-C_6H_4, $R^2 = R^3 = C_6H_5$; **3**, X = Br, $R^1 = R^2 = R^3 = C_6H_5$; **4**, X = Br, R^1 = p-CH_3-C_6H_4, $R^2 = R^3 = C_6H_5$; **5**, X = Cl, $R^1 = R^2 = C_6H_5$, $R^3 = CH_3$; **6**, X = Br, $R^1 = R^2 = C_6H_5$, $R^3 = CH_3$) with the expected ketenimine C=N bonding mode. Reduction of **1** with 1 equiv of Na/Hg gives the complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,N)\text{-}PhN{=}C{=}CPh_2)$ (**9**) as a paramagnetic compound. The reduction of **9** with 1 equiv of Na/Hg and the subsequent addition of a proton source (ethanol) leads to the iminoacyl compound $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CRNR^1)$ (**10**, R = $CH(Ph_2)$, R^1 = Ph). The one- and two-electron reductions of **1** have been studied by cyclic voltammetry experiments. The structure of **1** was determined by single-crystal X-ray diffractometry: a = 24.4904 (14) Å, b = 11.0435 (04) Å, c = 26.6130 (15) Å, β = 109.890 (5)°, monoclinic, space group $C2/c$, Z = 8, V = 6768.4 (5) Å^3, ρ_{calcd} = 1.3194 g/mL, R = 0.048, R_w = 0.060 based on 4806 observed reflections. The structure contains a niobium atom bonded to two cyclopentadienyl rings in a η^5 fashion; the coordination of the metal is completed by a Cl atom and a η^2(C,N)-bonded ketenimine ligand.

Introduction

The preparative usefulness of organometallic complexes as new reagents in organic syntheses has been increasing in the recent years.[1] Ketenes, ketenimines, and related heterocumulenes are very reactive organic molecules whose typical reactivity patterns are well-defined.[2] Several

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[†] Departamento de Quîmica Inorgânica.

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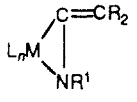
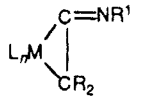
(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Vol. III, p 669.

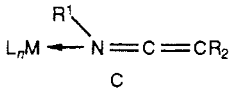
studies[3] provide information about the bonding modes of these compounds to different metal fragments, because metal-promoted transformations of them can simulate the metal-induced transformations on carbon dioxide, the activation of which is a matter of great interest.[4] Furthermore, transition-metal ketene complexes have been suggested as intermediates for the Fischer–Tropsch conversion of synthesis gas (CO/H_2) to hydrocarbons[5] and ketene or ketenimine complexes have been used as versatile synthetic building blocks. For example, ketenimine complexes have proven to be useful in new synthetic approaches to carbocyclic and four-, five-, and six-membered N-heterocyclic rings.[3b] Heterocumulenes are also known to bind to transition-metal centers in several ways. With π complexes, the coordination with a metal fragment, ML_n, can take place via the C=N or C=C π bonds (side on; A, B) or via the nitrogen lone pair (end on; C) and in all cases coordination brings about a great change in the reactivity of the ketenimine.



A



B



C

Ketenimine complexes have been previously prepared by C—C coupling reactions within the ligand sphere of transition metals: e.g. by reacting carbene or carbyne[6] complexes with isocyanides. In only a few cases have ketenimine complexes been prepared directly by coordination of free ketenimines.[7]

In our group, we have studied the chemistry of bis(cyclopentadienyl)niobium complexes with trimethylsilyl-substituted cyclopentadienyl ligands and have found that the carbenoid-like 16-electron species $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X$ reacts with heterocumulenes, such as PhNCO, to give complexes in which the heterocumulene is coordinated to the metal center.[8] We have continued to develop the chemistry of those niobium(III) complexes along the lines of (i) reactions with ketene and (ii) reactions with ketenimine ligands. This paper will focus on the preparation, reactivity, and structural details of η^2(*C,N*)-ketenimine–niobocene complexes. Electrochemical data are also discussed.

Results and Discussion

Synthesis and Properties. The reactions between $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X$ and ketenimines lead to the desired ketenimine complexes (eq 1) in high yields (ca. 80%). The

$$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X + R^1N{=}C{=}CR^2R^3 \rightarrow Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}R^1NCCR^2R^3) \quad (1)$$

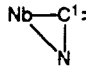
1–6

1, X = Cl, $R^1 = R^2 = R^3 = C_6H_5$; **2**, X = Cl, $R^1 = p\text{-}CH_3\text{-}C_6H_4$, $R^2 = R^3 = C_6H_5$; **3**, X = Br, $R^1 = R^2 = R^3 = C_6H_5$; **4**, X = Br, $R^1 = p\text{-}CH_3\text{-}C_6H_4$, $R^2 = R^3 = C_6H_5$; **5**, X = Cl, $R^1 = R^2 = C_6H_5$, $R^3 = CH_3$; **6**, X = Br, $R^1 = R^2 = C_6H_5$, $R^3 = CH_3$

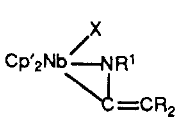
complexes were isolated as red air-stable solids that could be obtained as microcrystals from *n*-hexane or *n*-pentane. They are very soluble in common organic solvents to give deep red air-stable solutions, and we have also observed that the *p*-tolyl-substituted derivatives are considerably more soluble and tend to oil out from nonpolar solvents. Complexes **1–6** are diamagnetic. They have been characterized by standard analytical methods.

IR data are particularly informative regarding the bonding exhibited in transition-metal ketenimine complexes. The IR spectra of free ketenimines show a strong band at ca. 2050–2000 cm^{-1}. In our complexes the ν(N=C=C) band appears[9] at ca. 1580 cm^{-1} and this value agrees with the bathochromic shift reported for other π-bonded ketenimine complexes;[3] on the basis of these data neither η^2(C,N) nor η^2(C,C) coordination modes can be excluded. The X-ray crystal structure determined for **1** has confirmed the η^2(C,N) coordination mode in our complexes.

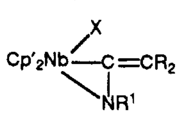
^1H NMR spectra show resonances corresponding to both the cyclopentadienyl rings and the ketenimine ligand. It must be noted that the average mean value corresponding to the cyclopentadienyl hydrogen atoms is shifted downfield relative to that for bis(cyclopentadienyl)niobium(III) complexes, as has been observed in several niobium(V) cyclopentadienyl complexes.[10] Particularly significant are the observed ^{13}C NMR spectra, which show five resonances for the cyclopentadienyl carbon atoms.[10] In addition, the spectra show that the resonances of C^1 and C^2 atoms



shifted as compared to those of the free ketenimines.[11] Both ^1H and ^{13}C NMR data indicate the presence of only one isomer with both exo and endo possibilities:



exo



endo

The X-ray crystal structure has shown that crystalline **1** has the exo structure.

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(2) (a) Patai, S., Ed. *The Chemistry of Ketenes, Allenes and Related Compounds*; Wiley: New York, 1980. (b) Krow, G. R. *Angew. Chem.* **1971**, *83*, 455; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 435. (c) Ulrich, H. *Cycloaddition Reactions of Heterocumulenes*; Academic Press: New York, 1967.

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(6) (a) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954. (b) Kreiter, C. G.; Aumann, R. *Chem. Ber.* **1978**, *11*, 1223. (c) Aumann, R.; Heinen, H.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1986**, *119*, 3141. (d) Fischer, E. O.; Schambeck, W.; Kreissl, F. R. *J. Organomet. Chem.* **1979**, *169*, C27. (e) Fischer, E. O.; Schambeck, W. *J. Organomet. Chem.* **1980**, *201*, 311.

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(8) (a) Antiñolo, A.; Garcia-LLedó, S.; Martinez de Ilarduya, J.; Otero, A. *J. Organomet. Chem.* **1987**, *335*, 85. (b) Antiñolo, A.; Fajardo, M.; Jalón, F. A.; López Mardomingo, C.; Otero, A.; Sanz-Bernabé, C. *J. Organomet. Chem.* **1989**, *369*, 187.

(9) Notice that the IR ν(C=C=N) bands in complexes **1–6** are at values lower than that reported by Behrens.[7] However, it is common for heterocumulenes π-bonded to transition metals to have a large range of values[3] depending upon the nature of the heterocumulene ligand and the oxidation state of the metal center.

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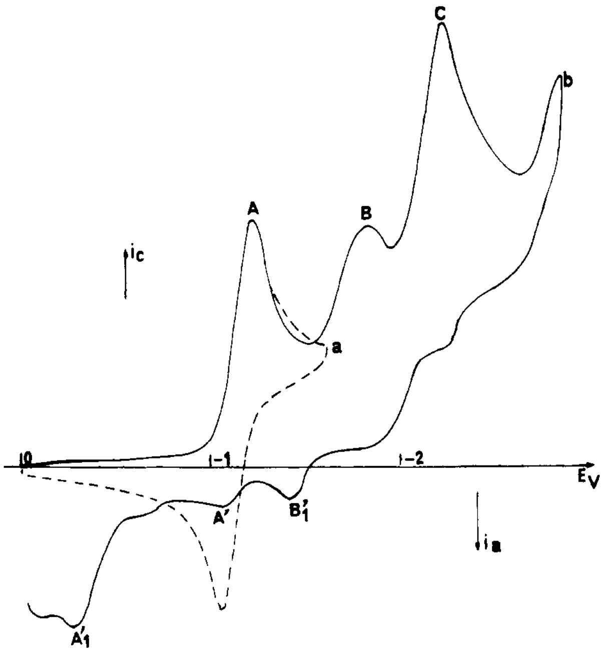
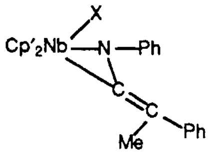
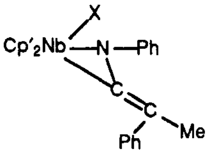


Figure 1. Cyclic voltammograms of Nb(η^5-$C_5H_4SiMe_3$)$_2$$Cl_2$ in THF (starting potential 0 V, sweep rate 0.2 V s^{-1}): (a) trace for the compound alone; (b) trace for the compound in the presence of 1 equiv of ketenimine ligand.

However, with unsymmetrical ketenimines isomeric mixtures are observed (via ^1H NMR spectroscopy) due to *E–Z* isomerism about the C=C bond:



exo-*E*



exo-*Z*

For **5** and **6** the *E*:*Z* ratios are 73:27 and 81:19, respectively; this assignment is based on the results previously reported[13b] for isoelectronic ketene–niobocene complexes.

Electrochemical Studies. We have previously discussed the mechanism of the electrochemical reduction of the niobium(IV) derivatives in which the cyclopentadienyl moiety is C_5H_5, $C_5H_4SiMe_3$, or 1,3-$C_5H_3(SiMe_3)_2$.[12] Thus, we now describe studies on the electrochemical behavior of compound **1**. In THF as solvent at a platinum electrode, the cyclic voltammogram of Nb(η^5-$C_5H_4SiMe_3$)$_2$$Cl_2$ exhibits a system of reversible peaks A/A'. In the presence of the ketenimine PhN=C=CPh_2, the two new reduction peaks B and C appear in the voltammogram. On the reverse scan oxidation peaks B'_1 and A'_1 are found along with the weak-intensity peak A' (Figure 1). Peak C corresponds to the reduction of the ketenimine ligand.

An electrolysis of the dichloride complex in the presence of 1 equiv of ketenimine carried out at −1.4 V, corresponding to the plateau of wave A, consumes 1 equiv of electrons. In cyclic voltammetry of the electrolyzed orange solution, reduction peaks B and C appear. Inversion of the potential scan after C produces the oxidation peak B'_1 (Figure 2). We have also studied the electrochemical behavior or complex **1**. Its voltammogram is identical with that displayed in Figure 3.

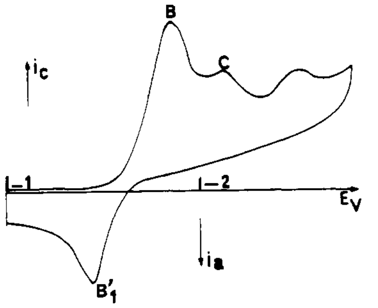


Figure 2. Cyclic voltammogram of Nb(η^5-$C_5H_4SiMe_3$)$_2$$Cl_2$ in THF after reduction at −1.4 V (consumption of 1 faraday/mol) in the presence of 1 equiv of ketenimine (starting potential −1.0 V, sweep rate 0.2 V s^{-1}). At lower cathodic potential, peak A'_1 is also observed.

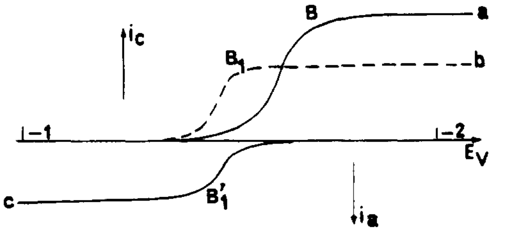


Figure 3. RDE voltammograms of **1** in THF on a platinum electrode (starting potential −0.6 V): (a) before electrolysis (an oxidation wave E'_1 at +0.24 V is also observed, which probably corresponds to the oxidated ligand); (b) after electrolysis at −2.0 V and consumption of 1 faraday/mol; (c) after two-electron reduction.

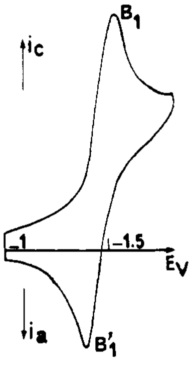


Figure 4. Cyclic voltammogram of **9** in THF (starting potential −1.0 V, sweep rate 0.2 V s^{-1}).

When the electrolysis of **1** is carried out at the potential of peak B, after consumption of 1 equiv of electrons the rotating-platinum-disk electrode (rde) voltammogram shows the reduction wave B_1, which is situated at a lower cathodic potential scan than wave B. If the electrolysis is pursued at the same oxidation potential, wave B'_1 is observed after the two-electron reduction (Figure 3). These results can be rationalized according to Scheme I. Peak A' corresponds to the oxidation of **7**. In the presence of the ketenimine, complex **1** is obtained. The formation of this niobium(V) derivative is in line with the Lewis base character of **7** (d^2 configuration) and the electrophilic character of ketenimine. We have observed that **7** rapidly reacts with the ligand, because when we have electrogenerated **7** after the ketenimine addition, the oxidation wave A' immediately disappeared and the reduction wave B was observed. The two-electron reduction of **1** yields the anionic species **8**, which is oxidized at the potential of the peak B'_1. On the time scale of controlled-potential electrolysis, after one-electron reduction the intermediate **9** is formed, which is reduced at the peak B_1 potential. The one-electron reduction of **9** gives **8**. We have studied the

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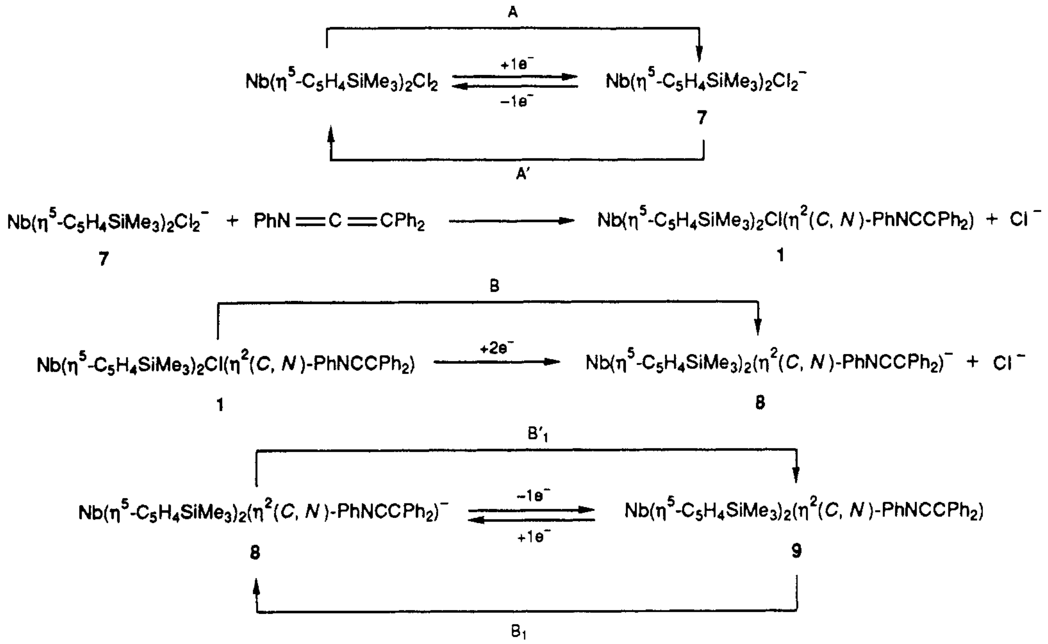
[13] (a) Otero, A.; Antiñolo, A.; Fajardo, M.; Jalón, F.; López-Mardomingo, C.; Sanz, C.; Florencio, F.; Sanz-Aparicio, J.; *Proc. Int. Conf. Organomet. Chem., 13th* **1988**, 188. (b) Halfon, S. E.; Fermin, M. C.; Bruno, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 5490.

Scheme I



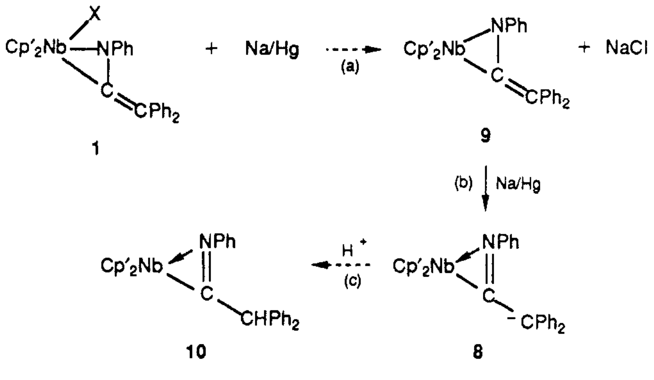
electrochemical behavior of chemically prepared 9 (see below). In THF as solvent the cyclic voltammogram exhibits the system of reversible peaks B_1/B'_1 (Figure 4).

The electrolysis of 9 at −1.6 V (0 °C) consumes 1 equiv of electrons, and the rde voltammogram of the red solution exhibits the wave B'_1, which corresponds to the oxidation of 8. 8 decomposes rapidly at room temperature, and the height of the oxidation wave B'_1 decreases and finally disappears. Also the formation of 9 during the electrolysis of 1 can be explained by an outer-sphere electron-transfer reaction between 8 and 1, since the potential difference is 300 mV. Compound 8 generated at the electrode diffuses toward the bulk of the solution and comes in contact with 1, which diffuses toward the electrode, and a reaction (eq 2) takes place.

$$\underset{8}{\mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}(C,N)\text{-}RNCCR_2)^-} + \underset{1}{\mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,N)\text{-}RNCCR_2)} \rightarrow \underset{9}{\mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,N)\text{-}RNCCR_2)} + \mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,N)\text{-}RNCCR_2)^- \quad (2)$$

In an effort to learn more about the properties of these ketenimine complexes and with the exhaustive information obtained via electrochemical experiments, we chose to investigate the reaction of 1 with a reducing agent such as Na/Hg. In fact, the reaction of 1 with 1 equiv of Na/Hg (one-electron process) leads to 9 (see Scheme II). 9 was isolated as a red-brown, highly air-sensitive microcrystalline solid from hexane or pentane solution and was characterized by standard analytical methods. Its IR spectrum shows the ν(N=C=C) band at 1554 cm^{-1}, corresponding to the presence of a η^2(*C*,*N*)-ketenimine group, which remains unchanged after the reduction process. 9 is paramagnetic, showing a complex EPR spectrum. The reason for this is that 1 undergoes in the first step (a) a one-electron reduction via a process involving loss of chloride without structural change in the ketenimine ligand. This behavior is different from that previously described.[13] In ketene–niobocene complexes, where the one-electron reduction leads to nioba enolate intermediates with a structural change in the ketene ligands. 9 reacts (step b) with 1 equiv of Na/Hg to give the unstable anionic iminoacyl complex 8 (as indicated by voltammetry experiments), which is easily protonated at the carbon atom, with ethanol as a proton source, to give the neutral iminoacyl complex 10 (step c). 10 was isolated as a highly air-sensitive green crystalline material, which was characterized spectroscopically. It turns out to be one of the few examples of niobocene species containing iminoacyl groups previously reported.[14] Further studies of the utility of the proposed intermediate 8 toward different reagents are in progress.

Scheme II



Cp′ = C$_5$H$_4$SiMe$_3$

X-ray Structure Determination of Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl(η^2(*C*,*N*)-PhN=C=CPh$_2$). The molecular geometry of 1 is depicted together with the atomic numbering in Figure 5.[15] The atomic coordinates and the equivalent isotropic temperature factors, with estimated deviations, are shown in Table I, while bond lengths and main bond angles are given in Table II.

Complex 1 crystallizes as red prisms with monoclinic symmetry, space group *C*2/*c*, and eight molecules per unit cell, which are monomeric units. The two cyclopentadienyl rings (Cp), which are bonded to the niobium atom in a true η^5 fashion, define an angle of 130° between their centroids,

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[14] Martinez de Ilarduya, J. M.; Otero, A.; Royo, P. *J. Organomet. Chem.* **1988**, *340*, 187.

[15] Motherwell, W. D. S.; Clegg, W. PLUTO: Program for Plotting Molecular and Crystal Structures; University of Cambridge: Cambridge, England, 1978.

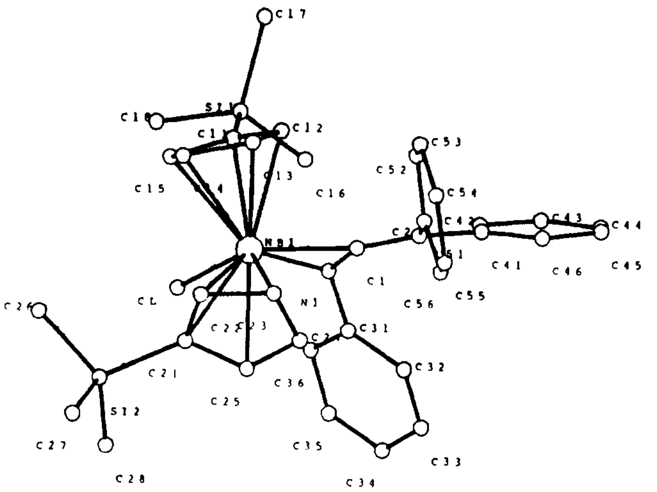

Figure 5. PLUTO view of 1 showing the atomic numbering scheme.

Table I. Atomic Parameters for 1

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Nb	0.302 79 (2)	0.404 41 (3)	0.379 06 (1)	329 (2)
Cl	0.265 22 (7)	0.260 19 (13)	0.302 12 (5)	583 (6)
Si1	0.417 00 (7)	0.349 85 (14)	0.307 09 (6)	506 (6)
Si2	0.134 31 (9)	0.383 26 (22)	0.300 56 (8)	735 (8)
N	0.353 54 (18)	0.251 28 (34)	0.417 27 (16)	369 (14)
C1	0.367 73 (23)	0.342 59 (39)	0.452 08 (18)	366 (16)
C2	0.403 73 (23)	0.367 27 (41)	0.503 03 (18)	393 (16)
C11	0.372 54 (25)	0.452 73 (47)	0.334 18 (20)	440 (18)
C12	0.392 08 (25)	0.510 69 (42)	0.384 64 (19)	417 (18)
C13	0.350 71 (28)	0.599 38 (45)	0.385 92 (23)	495 (21)
C14	0.306 51 (33)	0.602 15 (53)	0.334 78 (27)	603 (24)
C15	0.319 52 (29)	0.510 89 (55)	0.304 14 (22)	539 (21)
C16	0.439 18 (35)	0.207 96 (70)	0.345 69 (31)	682 (28)
C17	0.483 73 (37)	0.437 02 (77)	0.313 55 (32)	727 (31)
C18	0.374 61 (41)	0.320 01 (89)	0.235 46 (28)	801 (32)
C21	0.198 26 (24)	0.408 09 (55)	0.362 77 (21)	474 (19)
C22	0.220 33 (28)	0.522 20 (55)	0.384 99 (26)	542 (22)
C23	0.259 88 (27)	0.503 82 (66)	0.438 03 (24)	569 (23)
C24	0.259 49 (27)	0.382 33 (67)	0.449 52 (22)	544 (22)
C25	0.224 63 (24)	0.321 28 (54)	0.403 99 (21)	476 (19)
C26	0.145 35 (45)	0.446 14 (102)	0.240 48 (35)	929 (36)
C27	0.076 88 (46)	0.472 65 (195)	0.313 86 (58)	1312 (66)
C28	0.117 48 (56)	0.218 02 (106)	0.292 02 (44)	1078 (45)
C31	0.340 48 (23)	0.131 76 (40)	0.428 06 (21)	400 (18)
C32	0.344 51 (26)	0.095 85 (49)	0.479 33 (25)	495 (21)
C33	0.330 23 (33)	-0.023 01 (56)	0.488 59 (32)	626 (28)
C34	0.310 90 (37)	-0.103 74 (53)	0.447 01 (41)	751 (36)
C35	0.307 27 (34)	-0.069 57 (51)	0.396 97 (36)	702 (30)
C36	0.323 11 (29)	0.048 36 (51)	0.386 55 (27)	560 (23)
C41	0.451 33 (23)	0.286 55 (43)	0.534 72 (19)	401 (16)
C42	0.475 94 (28)	0.199 17 (58)	0.511 04 (24)	547 (21)
C43	0.522 22 (29)	0.129 85 (64)	0.541 23 (29)	628 (25)
C44	0.543 93 (33)	0.141 64 (75)	0.596 74 (30)	721 (27)
C45	0.520 93 (33)	0.227 37 (76)	0.619 88 (26)	723 (27)
C46	0.474 53 (30)	0.298 54 (63)	0.590 29 (25)	605 (23)
C51	0.395 59 (22)	0.482 82 (45)	0.528 44 (18)	394 (16)
C52	0.421 80 (28)	0.590 78 (49)	0.522 39 (22)	512 (20)
C53	0.412 49 (32)	0.696 54 (55)	0.545 84 (27)	614 (24)
C54	0.378 52 (38)	0.696 85 (66)	0.578 00 (29)	701 (28)
C55	0.352 95 (33)	0.591 55 (80)	0.585 70 (24)	681 (27)
C56	0.361 82 (27)	0.484 64 (61)	0.561 58 (22)	527 (21)

[a] $U_{eq} = 10^4[{}^1/_3\sum U_{ij}a_i^*a_j^*a_ia_j(\cos a_ia_j)]$.

both planes making a dihedral angle of 49.0 (3)°. The orientation of the two cyclopentadienyl rings is nearly eclipsed, with both $SiMe_3$ groups located at contiguous carbon atoms. Nb–C and C–C bond lengths in the two rings are in the usual range, the niobium atom being 2.141 (1) and 2.123 (1) Å, respectively, from the mean plane defined by Cp1 and Cp2. The most interesting aspect of the structure is found in the bonding between the metal and the coordinated ketenimine. In fact, the ketenimine moiety exhibits an η^2(C,N) coordination mode and the following features are of primary importance: N1–C1 = 1.333 (6) Å; C1–C2 = 1.370 (6) Å; N1–C1–C2 = 140.0 (4)°. These values are in accordance with those previously reported[7,16] in other η^2(*C*,*N*)-ketenimines. Both the ketenimine ligand and the chloride atom are situated in such a way that C2 and C1 atoms are 0.002 (6) and 0.039 (2) Å, respectively, from the plane defined by Nb,N1,C1. Packing in the unit cell is assured by van der Waals forces only. There are no significant intermolecular contacts.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for 1

Bond Distances			
Nb-Cp1	2.133 (1)	Nb-C12	2.441 (6)
Nb-Cp2	2.116 (1)	Nb-C13	2.429 (5)
Nb-Cl	2.509 (1)	Nb-C14	2.498 (6)
Nb-N	2.140 (4)	Nb-C15	2.466 (7)
Nb-C1	2.161 (4)	Nb-C21	2.447 (6)
N-C1	1.333 (6)	Nb-C22	2.452 (7)
N-C31	1.410 (6)	Nb-C23	2.428 (7)
C1-C2	1.370 (6)	Nb-C24	2.460 (7)
C2-C41	1.482 (6)	Nb-C25	2.411 (6)
C2-C51	1.489 (7)	Si1-C11	1.879 (6)
Nb-C11	2.453 (7)	Si2-C21	1.872 (5)
Bond Angles			
Cp2-Nb-C1	98.6 (1)	Nb-N-C1	72.8 (3)
Cp2-Nb-N	109.6 (1)	C1-N-C31	126.2 (4)
Cp2-Nb-Cl	104.9 (4)	Nb-C1-N	71.1 (3)
Cp1-Nb-C1	103.5 (1)	N-C1-C2	140.0 (4)
Cp1-Nb-N	114.9 (1)	Nb-C1-C2	148.9 (3)
Cp1-Nb-Cl	102.5 (3)	C1-C2-C51	118.6 (4)
Cp1-Nb-Cp2	129.8 (2)	C1-C2-C41	124.1 (4)
N-Nb-C1	36.1 (2)	C41-C2-C51	117.3 (4)
Cl-Nb-C1	119.1 (1)	Nb-C11-Si1	130.2 (3)
Cl-Nb-N	83.0 (1)	Nb-C21-Si2	131.6 (3)
Nb-N-C31	134.5 (4)		

Conclusion

We report in this paper new η^2(*C*,*N*)-ketenimine complexes that are easily prepared by direct coordination of ketenimine ligands. We found by both chemical and electrochemical methods that one- or two-electron reduction processes constitute a means of preparing a new class of niobocene derivatives. Future papers will report that reactivity of iminoacyl anions and related compounds toward several electrophilic reagents.

Experimental Section

All reactions were performed by using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen or argon. Solvents were distilled from appropriate drying agents and degassed before use.

Elemental analyses were performed with a Perkin-Elmer 240B microanalyzer. NMR spectra were recorded on a Varian FT 80A instrument. Chemical shifts are reported (δ) from $SiMe_4$. IR spectra were recorded as Nujol mulls between CsI plates in the region 4000–200 cm^{-1} with a Perkin-Elmer PE883 IR spectrometer. In the electrochemical experiments, a calomel-saturated reference electrode, separated from the solution by a sintered-glass disk, was used. The auxiliary electrode was a platinum-disk electrode. In all cases the supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.2 M); the salt (Fluka) was dried and deoxygenated before use. A Tacussel UAP4 unit connected to a Tektronix oscilloscope (linear potential sweep experiments), a three-electrode Tacussel Tipol polarograph, an Amel 552 potentiostat, and a Tacussel IG 5 integrator were used.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X$ (X = Cl, Br) and ketenimine ligands were prepared according to published methods.[8,17]

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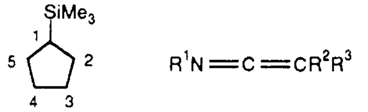
Nb(η^5-$C_5H_4SiMe_3$)$_2$X(η^2(*C,N*)-$R^1N{=}C{=}R^2R^3$) (X = Cl, R^1 = R^2 = R^3 = C_6H_5 (1); X = Cl, R^1 = *p*-CH_3-C_6H_4, R^2 = R^3 = C_6H_5 (2); X = Br, R^1 = R^2 = R^3 = C_6H_5 (3); X = Br, R^1 = *p*-CH_3-C_6H_4, R^2 = R^3 = C_6H_5 (4); X = Cl, R^1 = R^2 = C_6H_5, R^3 = CH_3 (5); X = Br, R^1 = R^2 = C_6H_5, R^3 = CH_3 (6)). To a brown solution of Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl (500 mg, 1.24 mmol) in 50 mL of hexane or pentane was added 335 mg (1.24 mmol) of $PhN{=}C{=}CPh_2$. The mixture was stirred for 2 h at room temperature. The solution became increasingly deep red, and it was then concentrated to ca. 5 mL. Red crystals of **1**, obtained by cooling, were collected and dried under vacuum; yield 700 mg (84%). Derivatives **2**–**6** were obtained by identical procedures.

1: IR (Nujol) $\nu(N{=}C{=}C)$ 1578 cm^{-1}; ^1H NMR (C_6D_6) δ 0.24 (s, 18 H, Si*Me*$_3$), 5.41 (2 H), 5.75 (2 H), 5.86 (2 H), 6.04 (2 H), each a complex signal, C_5H_4), 7.40–6.86 (mc, 15 H, *Ph*N=C=C*Ph*$_2$); $^{13}C\{^1H\}$ NMR (THF) δ 0.6 (Si*Me*$_3$), 117.5 (C^1), 108.5, 108.5, 122.6, 124.5 (C^2, C^3, C^4, C^5; exact assignment not possible), 152.9 (*C*NPh), 110.5 (*C*Ph$_2$), 147.5, 146.6, 143.5 (C_{ipso} of phenyl groups), 132.9, 130.6, 129.8, 129.2, 128.9, 127.8, 127.6, 123.7, 122.3 (C phenyl groups).



Anal. Found (calcd for $C_{36}H_{41}ClNNbSi_2$): C, 64.66 (64.34); H, 5.02 (6.10); N, 2.12 (2.08).

2: IR (Nujol) $\nu(N{=}C{=}C)$ 1583 cm^{-1}; ^1H NMR (C_6D_6) δ 0.26 (s, 18 H, Si*Me*$_3$), 5.29 (4 H), 5.52 (2 H), 6.03 (2 H) (each a complex signal, C_5H_4), 2.08 (s, 3 H, $CH_3C_6H_4$), 7.15 (mc, 14 H, $CH_3C_6H_4$ and Ph); $^{13}C\{^1H\}$ NMR (THF) δ 0.6 (Si*Me*$_3$), 117.9 (C^1), 107.8, 108.0, 122.6, 124.3 (C^2, C^3, C^4, C^5; exact assignment not possible), 152.8 (*C*N-*p*-tolyl), 110.3 (=*C*Ph$_2$), 143.4, 145.1, 146.5, (C_{ipso} of phenyl groups), 21.3 ($C_6H_4CH_3$), 135.6, 133.2, 131.2, 129.9, 129.3, 128.8, 128.4, 127.8, 126.5 (C phenyl groups). Anal. Found (calcd for $C_{37}H_{43}ClNNbSi_2$): C, 64.71 (64.77); H, 6.22 (6.27); N, 2.13 (2.04).

3: IR (Nujol) $\nu(N{=}C{=}C)$ 1579 cm^{-1}; ^1H NMR (C_6D_6) δ 0.10 (s, 18 H, Si*Me*$_3$), 5.00 (2 H), 5.24 (2 H), 5.36 (2 H), 6.06 (2 H), (each a complex signal, C_5H_4), 7.21 (mc, 15 H, *Ph*N=C=C*Ph*$_2$); $^{13}C\{^1H\}$ NMR (THF) δ 0.5 (Si*Me*$_3$), 119.4 (C^1), 107.6, 108.1, 123.9, 124.9 (C^2, C^3, C^4, C^5; exact assignment not possible), 146.7 (*C*NPh), 118.1 (=*C*Ph$_2$), 142.3, 143.1, 145.8 (C_{ipso} of phenyl groups), 133.0, 130.7, 129.9, 129.3, 128.8, 127.5, 127.3, 126.5 (C phenyl groups). Anal. Found (calcd for $C_{36}H_{41}BrNNbSi_2$): C, 60.03 (60.41); H, 5.89 (5.73); N, 2.29 (1.95).

4: IR (Nujol) $\nu(N{=}C{=}C)$ 1599 cm^{-1}; ^1H NMR (C_6D_6) δ 0.16 (s, 18 H, Si*Me*$_3$), 5.07 (2 H), 5.24 (2 H), 5.44 (2 H), 6.14 (2 H) (each a complex signal, C_5H_4), 1.97 (s, 3 H, $CH_3C_6H_4$), 7.01 (mc, 14 H, $CH_3C_6H_4$ and Ph); $^{13}C\{^1H\}$ NMR (THF) δ 0.8 (Si*Me*$_3$), 119.1 (C^1), 107.4, 108.0, 123.8, 124.7 (C^2, C^3, C^4, C^5; exact assignment not possible), 148.9 (*C*N-*p*-tolyl), 118.2 (=*C*Ph$_2$), 143.2, 144.9, 146.5 (C_{ipso} of phenyl groups), 21.3 ($C_6H_4CH_3$), 133.1, 132.8, 131.2, 129.8, 128.7, 128.2, 127.7, 127.4, 126.4 (C phenyl groups). Anal. Found (calcd for $C_{37}H_{43}BrNNbSi_2$): C, 60.88 (60.83); H, 5.96 (5.89); N, 1.99 (1.91).

5: IR (Nujol) $\nu(N{=}C{=}C)$ 1580 cm^{-1}; ^1H NMR (C_6D_6; **5a** (*E* isomer)) δ 0.26 (s, 18 H, Si*Me*$_3$), 2.4 (s, 3 H, CH_3), 5.30 (2 H), 5.63 (2 H), 6.00 (2 H), 6.31 (2 H) (each a complex signal, C_5H_4), 7.23 (mc, 10 H, C_6H_5); ^1H NMR (C_6D_6; **5b** (*Z* isomer)) δ 0.29 (s, 18 H, Si*Me*$_3$), 2.6 (s, 3 H, CH_3), 5.38 (2 H), 5.72 (2 H), 6.2 (2 H), 6.81 (2 H), (C_5H_4), 7.3 (mc, 10 H, C_6H_5). Anal. Found (calcd for $C_{31}H_{39}ClNNbSi_2$): C, 59.90 (61.04); H, 6.81 (6.39); N, 2.50 (2.99).

6: IR (Nujol) $\nu(N{=}C{=}C)$ 1579 cm^{-1}; ^1H NMR (C_6D_6; **6a** (*E* isomer)) δ 0.25 (s, 18 H, Si*Me*$_3$), 2.3 (s, 3 H, CH_3), 4.98 (2 H), 5.65 (4 H), 6.16 (2 H) (C_5H_4), 7.23 (mc, 10 H, Ph); ^1H NMR (C_6D_6; **6b** (*Z* isomer)) δ 0.19 (s, 18 H, Si*Me*$_3$), 2.19 (s, 3 H, CH_3), 5.15 (2 H), 5.9 (2 H), 6.23 (4 H) (C_5H_4), 7.23 (mc, 10 H, Ph). Anal. Found (calcd for $C_{31}H_{39}BrNNbSi_2$): C, 56.59 (56.88); H, 6.26 (5.96); N, 1.94 (2.14).

Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,N*)-$PhN{=}C{=}CPh_2$) (9). A mixture of **1** (500 mg, 0.8 mmol) and Na/Hg (0.8 mmol) in 50 mL of THF was stirred vigorously for 3 h at room temperature and then filtered and the red solution evaporated to dryness under vacuum. Hexane was used to extract the solid, and the resulting solution was concentrated to 10 mL. Red-brown needle crystals were obtained by cooling, which were collected and dried under vacuum; yield 350 mg (75%). **9**: IR (Nujol) ν(N=C=C 1554 cm^{-1}. Anal. Found (calcd for $C_{36}H_{41}NNbSi_2$): C, 67.27 (67.93); H, 6.32 (6.44); N, 2.25 (2.20).

Table III. Data for the X-ray Diffraction Analyses of 1

formula	$C_{36}H_{41}NSi_2ClNb$
mol mass, g/mol	672.258
space group	*C*2/*c*, monoclinic
a, Å	24.4904 (14)
b, Å	11.0435 (04)
c, Å	26.6130 (15)
α, deg	90.000 (0)
β, deg	109.890 (5)
γ, deg	90.000 (0)
Z	8
V, Å^3	6768.4 (5)
ρ(calcd), g/mL	1.3194
color	red prisms
temp, °C	25
abs coeff, μ, cm^{-1}	45.748
diffractometer	four-circle, Philips PW 1100
monochromator	graphite oriented
radiation (λ, Å)	Cu Kα (1.54178)
no. of rflns measd	5020
no. of rflns obsd	4806 (2σ(*I*) criterion)
R	0.048
R_w	0.060

Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,N*)-$PhN{=}C{-}CHPh_2$) (10). A mixture of **9** (300 mg, 0.52 mmol) and Na/Hg (0.52 mmol) in 50 mL of THF was stirred vigorously for 3 h at room temperature and then filtered, ethanol (1 mL) was added to the reddish green solution, and a green color developed. This solution was evaporated to dryness, hexane was used to extract the solid, and the resulting solution was concentrated to 5 mL. Deep green crystals were obtained on standing for 24 h at −20 °C, which were collected and dried under vacuum; yield 250 mg (83%). **10**: IR (Nujol) $\nu(N{=}C)$ 1636 cm^{-1}; ^1H NMR (C_6D_6) δ 0.19 (s, 18 H, Si*Me*$_3$), 3.68 (2 H), 3.84 (2 H), 5.06 (2 H), 5.52 (2 H) (each a complex signal, C_5H_4), 2.09 (s, 1 H, C*H*Ph$_2$), 7.04 (mc, 15 H, Ph); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 1.98 (Si*Me*$_3$), 110.6 (C^1), 98.3, 101.18, 103.2, 111.5 (C^2, C^3, C^4, C^5; exact assignment not possible), 32.3 (*C*HPh$_2$), 139.9, 142.5, 145.3 (C_{ipso} of phenyl groups), 127.9, 128.1, 129.3, 129.5, 129.7, 129.9, 130.1 (C phenyl groups), *C*=N was not observed. Anal. Found (calcd for $C_{36}H_{42}NNbSi_2$): C, 67.42 (67.82); H, 6.04 (6.59); N, 2.38 (2.19).

X-ray Structure Determination. Crystal data and the data collection procedure are shown in Table III. In the reduction of the data, Lorentz and polarization factors were applied and absorption effects were corrected.[18]

The niobium atom position was found from a Patterson map, while the remaining non-H atoms were located by subsequent Fourier synthesis. Refinement was carried out with full-matrix least squares, first with isotropic temperature factors and later on with anisotropic thermal parameters. H atoms were included in positions calculated geometrically and fixed. An empirical weighting[19] scheme was applied so as to give no trends in $\langle w(\Delta^2F)\rangle$ vs $\langle F_0\rangle$ and $\langle(\sin\theta)/\lambda\rangle$. Final mixed refinement gave R = 0.048 (R_w = 0.060); a final difference Fourier synthesis did not show any peak higher than 0.79 e Å^{-3}. Atomic scattering factors and anomalous dispersion corrections were taken from ref 20. Most calculations were performed with the X-Ray system[21] and Parst[22] on a Vax 11/750 computer.

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Organometallics **1990**, *9*, 2925–2933

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Registry No. **1**, 129571-38-6; **2**, 129571-39-7; **3**, 129571-40-0; **4**, 129571-41-1; *exo*-(*E*)-**5**, 129571-42-2; *exo*-(*Z*)-**5**, 129646-63-5; *exo*-(*E*)-**6**, 129571-43-3; *exo*-(*Z*)-**6**, 129646-64-6; **9**, 129571-44-4; **10**, 129571-45-5; $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$, 116852-35-8; $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br$, 125821-09-2; $C_6H_5N{=}C{=}C(C_6H_5)_2$, 14181-84-1; $p\text{-}CH_3C_6H_4B{=}C{=}C(C_6H_5)_2$, 5110-45-2; $C_6H_5B{=}C{=}C(CH_3)C_6H_5$, 32907-79-2.

Supplementary Material Available: Listings of fractional coordinates, anisotropic thermal parameters, all bond distances and bond angles, torsion angles, least-squares planes, and interatomic and intermolecular contacts for **1** and the EPR spectrum of **9** (23 pages); a listing of the observed and calculated structure factors for **1** (20 pages). Ordering information is given on any current masthead page.

Low-Temperature Photochemistry of Oxy-Substituted Trisilanes

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Several new oxy-substituted trisilanes $RO(Mes)Si(SiMe_3)_2$ were synthesized and photolyzed in hydrocarbon matrices at 77 K to give silylenes, RO(Mes)Si:. The silylenes with R = mesityl and 2,6-diisopropylphenyl showed UV spectra that varied with matrix viscosity, attributed to conformational changes as the silylene relaxed to its equilibrium geometry. The structures of the two hindered (aryloxy)trisilanes **2a** and **2c** were determined by X-ray crystallography. Crystal data: **2c**, R = phenyl, $a = 16.609$ (3) Å, $b = 18.081$ (3) Å, $c = 20.029$ (3) Å, orthorhombic, *Pbca*, $Z = 8$; **2a**, R = 2,6-diisopropylphenyl, $a = 13.078$ (2) Å, $b = 12.054$ (3) Å, $c = 15.111$ (3) Å, $\beta = 102.05$ (1)°, monoclinic, $P2_1/c$, $Z = 4$. Their geometries about the central silicon atom were related to the UV properties of their respective silylenes. The solution-phase irradiation of the trisilane with R = 2,6-diisopropylphenyl at −60 °C led to the isolation of the first heteroatom-substituted cyclotrisilane, $[RO(Mes)Si]_3$, whose structure was determined by X-ray crystallography: space group $P\bar{1}$, $a = 15.541$ (2) Å, $b = 17.707$ (3) Å, $c = 11.989$ (2) Å, $\alpha = 109.70$ (1)°, $\beta = 109.60$ (1)°, $\gamma = 78.86$ (1)°, $Z = 2$.

The understanding of silylene chemistry has increased significantly in the last decade with the application of matrix isolation techniques to the study of these very reactive species.[1] In this paper we report studies of several oxy-substituted silylenes, **3a–f**, obtained by the photolysis of the corresponding trisilanes **2a–f** at 77 K in hydrocarbon matrices and in solution at low temperatures.[2]

Results and Discussion

Synthesis of Oxy-Substituted Trisilanes. Linear trisilanes $RR'Si(SiMe_3)_2$, which are good photochemical precursors to silylenes,[1,2] can often be made by coupling dichlorosilanes $RR'SiCl_2$ with trimethylchlorosilane in THF as shown in eq 1.[3] However, attempts to make

$$RR'SiCl_2 + 2Me_3SiCl + 4Li \xrightarrow[0\ ^\circ C]{THF} RR'Si(SiMe_3)_2 \qquad (1)$$

oxy-substituted trisilanes by this route all failed. The oxy group was displaced in preference to Cl in some reactions, and in every case, the major trisilane product had no oxy group remaining. Synthesis of the appropriate trisilanes was achieved by starting from 2-mesityl-2-chloro-1,1,1,3,3,3-hexamethyltrisilane (**1**). For aryloxy-substituted trisilanes, the best results were obtained by reacting the (aryloxy)lithium reagent with **1** in THF as shown in eq 2.

$$ArO^-Li^+ + \underset{\mathbf{1}}{Mes(Cl)Si(SiMe_3)_2} \xrightarrow{THF} \underset{\mathbf{2a\text{–}2c}}{Mes(OAr)Si(SiMe_3)_2}$$

2a, Ar = 2,6-diisopropyl; **2b**, Ar = mesityl; **2c**, Ar = phenyl (2)

Table I. Absorption Maxima of Silylenes 3a–f in Various Matrices

	λ_{max}, nm	
silylene	3-MP	1:1 3-MP/isopentane
3a	430	398
3b	425	400
3c	400	400
3d	390	390
3e	395	395
3f	396	396

Use of alkoxide ions in place of aryloxide in the reaction shown by eq 3 led to cleavage of Si–Si bonds. Alkoxytrisilanes **2d–2f** were therefore synthesized by the reaction of the corresponding alcohol with **1** in the presence of Et_3N (eq 3).

$$\underset{\mathbf{1}}{Mes(Cl)Si(SiMe_3)_2} + ROH \xrightarrow{4Et_3N} \underset{\mathbf{2d\text{–}2f}}{Mes(OR)Si(SiMe_3)_2} \qquad (3)$$

2d, R = methyl; **2e**, R = ethyl; **2f**, R = *tert*-butyl

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[1] For examples of the use of matrix isolation techniques in silylene chemistry, see: (a) Drahnak, T., J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 5427. (b) Michalcyzk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, J. *Silicon, Germanium, Tin Lead Compd.* **1986**, *9*, 75. Sekiguchi, A.; Hagiwara, K.; Ando, W. *Chem. Lett.* **1987**, *1*, 209.

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